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EFFECTS OF THE LDEF ORBITAL ENVIRONMENT ON THE REFLECTANCE OF OPTICAL MIRROR MATERIALS

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ABSTRACT

Specimens of eight different optical mirror materials were flown in low earth orbit as part of the Long Duration Exposure Facility (LDEF) manifest to determine their ability to withstand exposure to the residual atomic oxygen and other environmental effects at those altitudes. Optical thin films of aluminum, gold, iridium, osmium, platinum, magnesium fluoride-overcoated aluminum and reactively deposited, silicon monoxide-protected aluminum, all of which were vacuum deposited on polished fused silica substrates, were included as part of Experiment S0010, Exposure of Spacecraft Coatings. Two specimens of polished, chemical vapor deposited (CVD) silicon carbide were installed in sites available in Experiment A0114, Interaction of Atomic Oxygen with Solid Surfaces at Orbital Altitudes, which included trays in two of the spacecraft bays, one on the leading edge and the other on the trailing edge. One of the silicon carbide samples was located in each of these trays.

This paper will compare specular reflectance data from the preflight and postflight measurements made on each of these samples and attempt to explain the changes in light of the specific environments to which the experiments were exposed.

INTRODUCTION

The scientific community has long been aware that the orbital space environment presents a unique set of ambient conditions for their flight instruments. There has been a determined effort, going back to the early Space Shuttle flights, to establish the ability of candidate materials to withstand this environment. Particular concern about some thin film coatings used for reflective optical elements led to the investigation by Gull and coworkers on the short-term, low earth orbit effects, as part of a series of experiments known as the Evaluation of Oxygen Interaction with Materials (EOIM).[1] Their selection of coatings was part of the contingent which was exposed during the second mission of this experiment, flown on Shuttle mission STS-8 from August 30 to September 5, 1983. During the following year, the opportunity to evaluate long-term effects on these coatings, as well as others, presented itself with the deployment of the Long Duration Exposure Facility (LDEF), with an intended flight duration of one year. However, due to changes in Shuttle schedule priorities, it was almost six years before the spacecraft was retrieved.

Eight optical coating materials were included in the complement furnished by the Goddard Space Flight Center (GSFC), most of which have application in the vacuum ultraviolet (VUV) portion of the electromagnetic spectrum and several which find primary use in instruments for the visible and near-UV regions.

EXPERIMENT DESCRIPTIONS

Seven test samples, all of which were vacuum deposited thin films on 25 mm diameter by 2.5 mm thick, polished fused silica substrates, were mounted in an aluminum tray with machined recesses to accommodate these samples as well as those provided by others. The tray was covered with an aluminum plate having circular openings concentric with those in the tray but of slightly smaller diameter so as to retain the samples while permitting their exposure to the orbital environment. The entire assembly was mounted in a container known as the Experiment Exposure Control Canister (EECC), which is an automated experiment container capable of opening and closing during the flight. This collection is part of LDEF experiment S0010, Exposure of Spacecraft Coatings. The moving section of the EECC system, which contains the sample platform, translates out of a sealed container to expose the samples in a manner similar to the opening of a drawer. Thus the system provides a means for maintaining a clean, low pressure or inert gas environment while closed during ground operations and delaying the exposure of the experiment until the spacecraft is in orbit.

The timer control circuitry for the EECC was set so that the drawer was in the open position for 10 months, so that despite the extended orbital period for the spacecraft, the materials in this experiment were only exposed to the space environment for the period of time originally intended. It was noted that the canister was still under partial vacuum just prior to its being opened to retrieve the samples. The system was mounted on the leading edge of the spacecraft, so that the normal to the sample surfaces was about 10° from the ram vector.

The thin films exposed as part of the EECC experiment were aluminum, gold, iridium, osmium, platinum, magnesium fluoride-overcoated aluminum, and aluminum overcoated with reactively deposited silicon monoxide (SiO_x). The source of each sample and the nominal film thicknesses are provided in Table I.

It was mentioned earlier that eight optical materials were furnished by GSFC for this flight. In addition to the seven already mentioned as being mounted in the EECC, two specimens of polished, chemical vapor deposited (CVD) silicon carbide, provided by Choyke of the Westinghouse Research and Development Center[2], were installed in sites available in another experiment package, A0114 (Interaction of Atomic Oxygen With Solid Surfaces at Orbital Altitudes), which included trays in two of the spacecraft bays, one on the leading edge and the other on the trailing edge. One of the SiC samples was located in each of the trays and they were exposed for the full duration of the flight. The samples, which were 16-mm long, 12-mm wide, and 0.25-mm thick, were masked by the tray's cover plate so as to shield 1/2 of their surfaces from the environment, the protected half serving as a control. The edges of the cutouts in the cover plate delineating the two halves of the samples were beveled to minimize shadowing effects from obliquely incident flux.

EXPERIMENTAL RESULTS

The wavelength range selected for reflectance measurements of a particular sample being studied depended on the typical usage of that coating and whether the measurement could provide some insight into the nature of the changes observed. Wavelengths varied from as low as 58 nm up to 20 micrometers. Reflectances at wavelengths below 100 nm were measured using a 2-m glancing incidence vacuum monochromator with a duoplasmatron light source. Measurements from 100 to 200 nm were made with a gaseous discharge light source mounted to a 1-m normal incidence vacuum monochromator. Each monochromator was fitted with a reflectometer of the type described by Hunter[3] in which the sample reflectances were measured at a 15° angle of incidence. Preflight near-UV and visible region reflectances were measured in a prism spectrophotometer equipped with an integrating sphere attachment, which provided the reflectance relative to a vacuum deposited aluminum standard. This instrument has since been replaced with a grating spectrophotometer with an absolute reflectance accessory, which may account for some of the reflectance differences between preflight and postflight measurements, since the absolute reflectance of the aluminum standard used with the original instrument was not documented at that time. This will be addressed where appropriate in the following discussion of the experimental results. A Fourier transform spectrometer was used to make IR reflectance measurements in the 2-20 micrometer wavelength region.

The recovered EECC experiment package was delivered intact to the NASA Langley Research Center, home installation of the principal investigator, where the canister was vented and preliminary visual examination of the specimens was conducted prior to their removal from the trays. Those noticeably changed were the osmium and gold samples.

Osmium

The appearance of the osmium sample was typical of what we had seen on previous low earth orbit exposures[1]. The film had become sufficiently transparent so that the identification number scribed on its back surface was visible from the front. Subsequent reflectance measurements, made after the samples had been removed from their tray and returned to GSFC, were essentially a duplication of earlier results and are shown graphically in Figure 1. As before, the postflight reflectance spectrum is characteristic of vacuum deposited chromium, again indicating that the osmium had disappeared, presumably by oxidation to its relatively volatile tetroxide, leaving behind the chromium binder layer.

Gold

Preliminary examination of the gold sample prior to removal from the EECC tray revealed an area that appeared to be lighter in color than the rest of the surface. This area was kidney-shaped, its longest dimension was about 2/3 that of the sample diameter, and it was somewhat eccentric while still including the sample center within its bounds. After retrieval of the sample and return to GSFC, it was microscopically examined in greater detail using Nomarski differential interference contrast at magnifications from as low as 3X to as high as 1,000X. This examination revealed that the surface outside the kidney-shaped area was considerably rougher than that inside. This was later verified using a Wyko TOPO-2D two-dimensional surface profiler. The measured RMS roughnesses of the outer and inner areas were 1.42 and 0.62 nm, respectively, compared to 0.43 nm for the control sample, which had been coated at the same time and was stored in the laboratory for the duration of the flight.

Normal incidence reflectance measurements at the center and edge of the sample over the wavelength region from 58 to 200 nm indicated substantial degradation of the coating. These data, presented in Figure 2, show that the reflectance of central area, within the kidney-shaped zone, decreased fairly uniformly over the entire spectral region, whereas that of the area outside this zone showed an additional decrease in the region above 100 nm, suggesting multiple degenerative phenomena.

In an attempt to understand the mechanisms of the observed degradation, reference was made to the work of others studying the modifications of material surface properties due to interaction with ambient atomic oxygen in low earth orbit, in particular, the work of Peters, et al[4], which included a study of gold films. They studied the physical removal of films by momentum imparted from collisions with incident atoms rather than chemical reactions, which represents the situation for gold since it sputters with relatively high yields and is not reactive with oxygen. Based on their sputtering yield of 5×10^{-5} for 5-ev oxygen atoms incident on gold, and a reported[5] oxygen fluence in the order of 10^{21} atoms/cm^2, we have estimated that several monolayers of gold could have been sputtered during the exposure period.

They also observed that etching in orbit is very sensitive to certain contaminants overlying the reactive materials, including silicones, which are not effectively removed by oxygen atoms. The presence of silicone contamination on our gold sample is a distinct possibility, since considerable amounts of contaminant found to contain silicone material were visible on the drawer guides and other external surfaces of the EECC and the position of the gold sample was immediately adjacent to one edge of the drawer.

On the basis of this information, one possible scenario for the observed degradation of the gold film involves creep of the silicone molecules onto its surface, moving from the tray cover toward the exposed center of the sample, where the contaminant layer would be expected to be thinnest. This layer would retard the sputtering action of the oxygen atoms most effectively at the periphery of the sample where its thickness is greatest, giving rise to a contaminated outside zone and an etched central portion. The displacement of the etched area away from the drawer edge could be explained by the directional source of the contaminant.

As part of the process of preparing the gold samples, the deposition monitor's reflectance was measured over the spectral range of 350-750 nm. Since gold coatings have application in the visible and IR as well as in the VUV, these measurements were repeated for the flight and control samples upon retrieval of LDEF, although instrumental geometry limited these to the centers of the samples. As we pointed out above, preflight and postflight measurements in this spectral region were made with different instruments. This may explain the difference between the preflight reflectance curve of the deposition monitor and the postflight reflectance of the control sample, as shown in Figure 3, although a portion or all of the change may be due to adsorption of ambient contaminants on the surface of the latter. More importantly though, the flight sample suffered substantial degradation, especially above 500 nm, when compared to the control, which is consistent with the visual appearance of its surface.

Platinum and Iridium

Both the platinum and iridium samples fared comparatively well, as shown in Figures 4 and 5. The largest of the changes exhibited by the Pt are about 2%, which is in the order of magnitude of the measurement accuracy and, therefore, it may be considered essentially unchanged. The Ir sample experienced losses of about 6% or less in the measured spectral range, which is very similar to the changes seen in the short term exposure in the EOIM experiment on STS-8, referred to previously. It appears that whatever is affecting the reflectance of the Ir, be it oxidation or some other phenomenon, occurs within a short time of its initial exposure to the orbital environment, after which the film seems rather stable. Surface roughness comparison with its control sample did not show any roughening of the flight specimen.

Aluminum

The bare, vacuum-deposited aluminum sample, unprotected by any dielectric overcoating, seems to have suffered significant reflectance degradation only in the wavelength region below 250 nm, presumably due to the oxidation of the aluminum to aluminum oxide, which is absorbing in the UV. As seen in Figure 6, the reflectance is essentially unchanged through the visible portion of the spectrum, although there is a slight decreasing trend, amounting to no more than a few percent toward the longer wavelengths. Since the oxidation of aluminum occurs rapidly upon its exposure to the atmosphere, after which its reflectance is relatively stable, the additional losses experienced, compared to the relatively small changes in the control sample, can probably be attributed to the greater reactivity of the atomic oxygen in low earth orbit relative to that of atmospheric, molecular oxygen. The reflectance losses observed are almost identical to that for the sample from the same deposition batch flown as part of the EOIM-II shuttle-borne experiment, indicating that these changes occurred early in the flight, i.e., within the first few days. The close agreement between preflight and postflight reflectance measurements in the visible tend to refute the earlier suggestion that instrumentation differences may have been responsible for some of the change observed for the gold sample.

Al + MgF_2

Magnesium fluoride-protected aluminum mirrors, commonly used in the vacuum ultraviolet (VUV) because of their high reflectance down to 110 nm, were flown as part of both the EOIM-II and LDEF contingents. Those in the former experiment were essentially unchanged with the exception of those samples which were obviously contaminated by discharges from other sources in the shuttle environment. The LDEF sample, on the other hand, which showed no visible evidence of having been contaminated, experienced significant reflectance degradation in the wavelength region around 150 nm, as seen in Figure 7. Studies have shown[6] that the presence of a thin absorbing film on the surface of an Al+MgF_2 mirror with a nominal MgF_2 thickness of 25 nm causes reflectance degradation in the wavelength vicinity of 200 nm, where the MgF_2 thickness corresponds to a 1/4-wave and the electric field at the mirror surface is at a maximum, thus resulting in the greatest sensitivity to thin contaminant layers. The substantial change in the 150 nm region suggests a plasma resonance absorption in aluminum enhanced by surface roughness[7], and although interferometric comparison of the flight and control samples indicated no significant difference in surface roughness, additional investigation of the surface is needed before a final assessment can be made.

Al + SiO_x

Al + SiO_x films are produced by overcoating the evaporated aluminum with silicon monoxide (SiO) at low deposition rates and relatively high pressures of oxygen or air, in order to produce films with low indices of refraction and negligible absorptance in the solar spectral region. During this reactive evaporation process, the ratio of evaporated SiO and oxygen molecules arriving simultaneously at the substrate surface is carefully controlled to obtain highly transparent films of a higher oxide.

The reflectance spectrum of the LDEF flight mirror sample so produced is compared with that of its control sample in Figure 8. Although this coating is not normally used at wavelengths as low as 160 nm, measurements were made in this region in an attempt to understand the nature of the environmentally induced changes. For the same reason, reflectances were also made in the 2 to 20-μm region and are plotted in Figure 9.

Examination of the data below 750 nm reveals a shift in the reflectance curve toward the shorter wavelengths, resulting in substantial increases below 300 nm. This effect is very much like that ascribed to UV irradiation of the films, a technique used to eliminate undesired UV absorptance of reactively deposited silicon oxide[8,9]. The infrared measurements show that the reduction in UV absorptance, while it may indicate a change in oxidative state, is not the result of the conversion of the SiO_x into SiO_2, since it did not produce a new absorption band at 12.5 μm, but may also be due to removal of dislocations and the production of a better defined stoichiometric order throughout the film[10].

Silicon Carbide

The reflectance changes exhibited by the two SiC samples, which were exposed for the full duration of the flight, are shown in Figs. 10 and 11. The exposed portion of the leading-edge sample suffered a drastic drop in reflectance over the wavelength range of 60-160 nm, whereas the losses of the trailing-edge sample were less than half as much over the same region. An analysis of these samples is being continued by the supplier, but a candidate mechanism for the gross loss observed is oxidation caused by direct exposure to the ram for an extended period, based on the similarity of the reflectance cutoff to that of silicon dioxide.

The recently published work of Seely et al.[11] supports this contention. They simulated the effects of exposures of up to 7.5 years in low earth orbit by bombarding SiC with oxygen atoms in the laboratory. Their analysis indicated that the reflectance reductions were due to an increase in thickness of a surface layer of SiO_x (where x is ~ 1.5) from 0.8-1.8 nm to 3.5-4.5 nm. Their measurements, which were consistent with x-ray photoelectron spectroscopy of the exposed mirrors, indicated that most of the growth in thickness of the SiO_x layers occurred during the first several years of simulated space exposure.

Examination of their calculated reflectance spectrum of a bombarded SiC mirror shows that the predicted values fall between those of the leading- and trailing-edge specimens in our flight experiment. Several possible explanations for the variance exist, including deviation of the assumed optical constants of the SiC substrate in their analysis from actual values, and a possible enhancement of the oxidation process in space due to simultaneous exposure to solar UV radiation.

DISCUSSION

It is clear from the results for these optical mirror materials that they reinforce the data obtained from the EOIM experiments. It has been shown that the low-earth-orbit environment can be a harsh setting for mirrors, particularly those that have proved useful in VUV applications. The mechanisms by which the optical materials degrade may not be fully understood and will require further analysis, but the indications are that atomic oxygen plays a significant role, either as a sputtering agent, as an oxidant, or both. The situation is complicated by evidence of contamination of various spacecraft and sample surfaces, some of which appear to be due to outgassing of sources within the structure. There is also an indication of unexpected thin layers of metallic species on specimen, as well as spacecraft, surfaces.[12]

In spite of remaining uncertainties about the mechanisms of the observed changes, the results strongly suggest the need for protecting optical surfaces against the external low-earth-orbit environment, particularly ram direction effects, although the degradation of some materials is not limited to surfaces in that orientation. The deterioration of the SiC mirror mounted on the trailing edge, while not as severe as that of its leading-edge counterpart, supports that contention, as do the results with Os oriented 180° to the ram vector in one of the earlier EOIM experiments.[13] The smaller, but significant, degradation of the masked portions of the LDEF SiC samples indicates the need for careful consideration in the design of optical instrumentation to protect the sensitive surfaces.

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Table 1. Optical Thin-Film Samples for the LDEF/EECC

Film Material	Source	Nominal Film Thicknesses (nm)[a]
Al	GSFC	70
Au	GSFC	10Cr + 10Cr/Au + 80Au
Os	ARC[b]	5-10 Cr + 20 Os
Ir	ARC	5-10 Cr + 17.5 Os
Pt	ARC	5-10 Cr + 20 Pt
Al + MgF_2	GSFC	70 Al + 25 MgF_2
Al + SiO_X	GSFC	70 Al + 180 SiO_X

[a]Chromium was used as a binder layer where indicated to improve adhesion between the top film and substrate. The GSFC process for Au includes an intermediate layer of codeposited Cr and Au to enhance adhesion further.

[b]Acton Research Corporation, Acton, Massachusetts

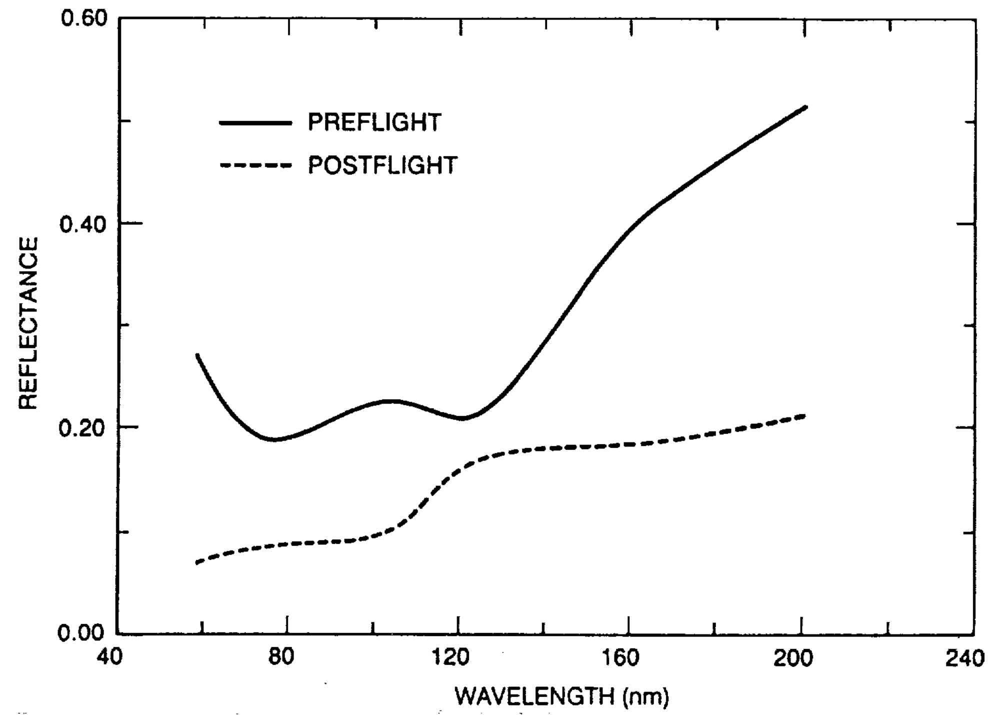

Figure 1. Effect of long duration, low earth orbit exposure on the VUV reflectance spectrum of an osmium film.

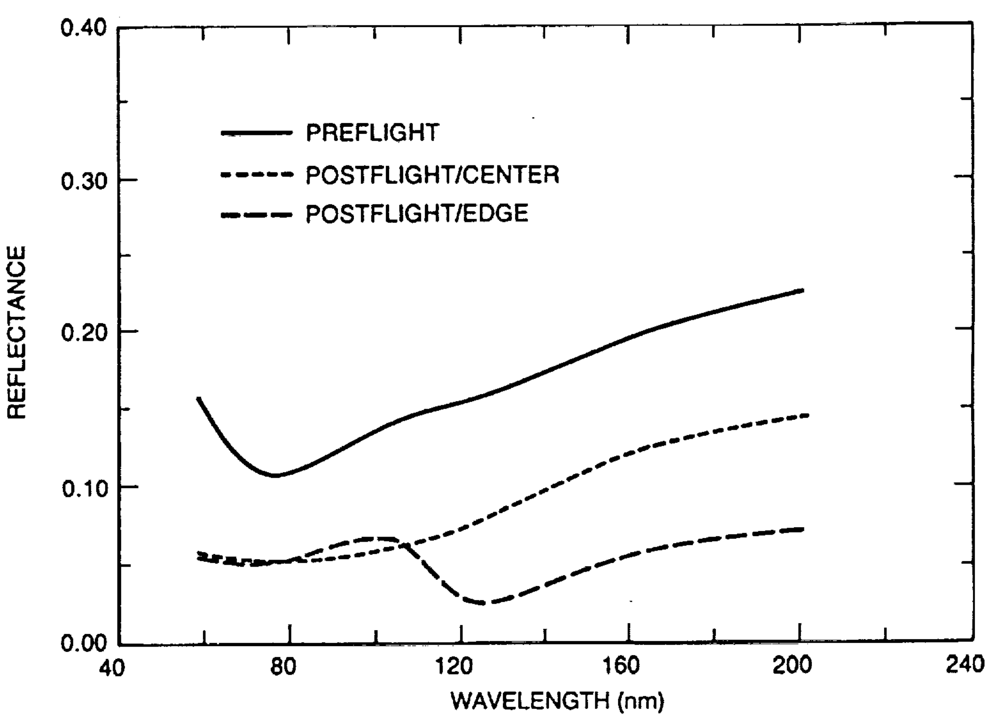

Figure 2. Effect of long duration, low earth orbit exposure on the VUV reflectance spectrum of a gold film.

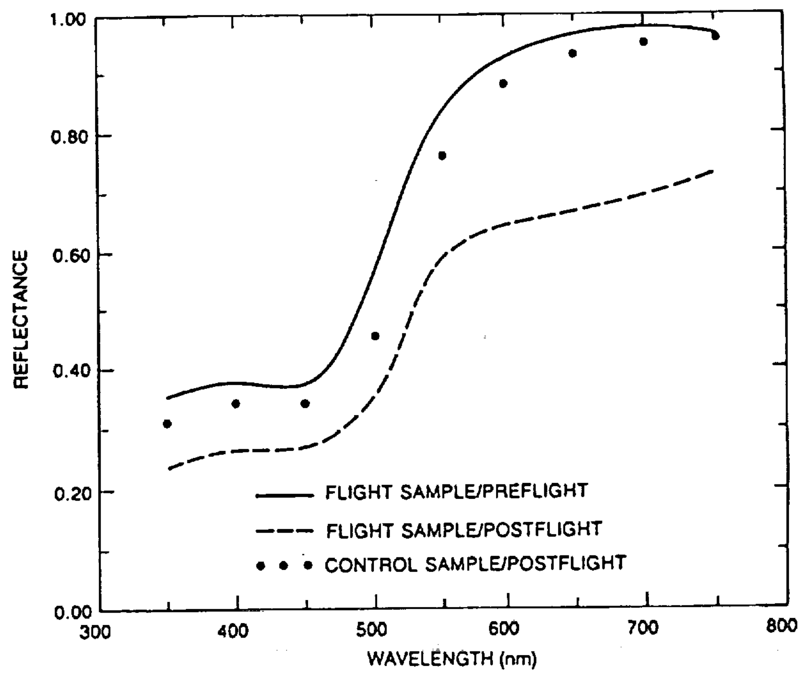

Figure 3. Comparison of visible wavelength spectra of the flight sample and a nonflight control sample of a gold film.

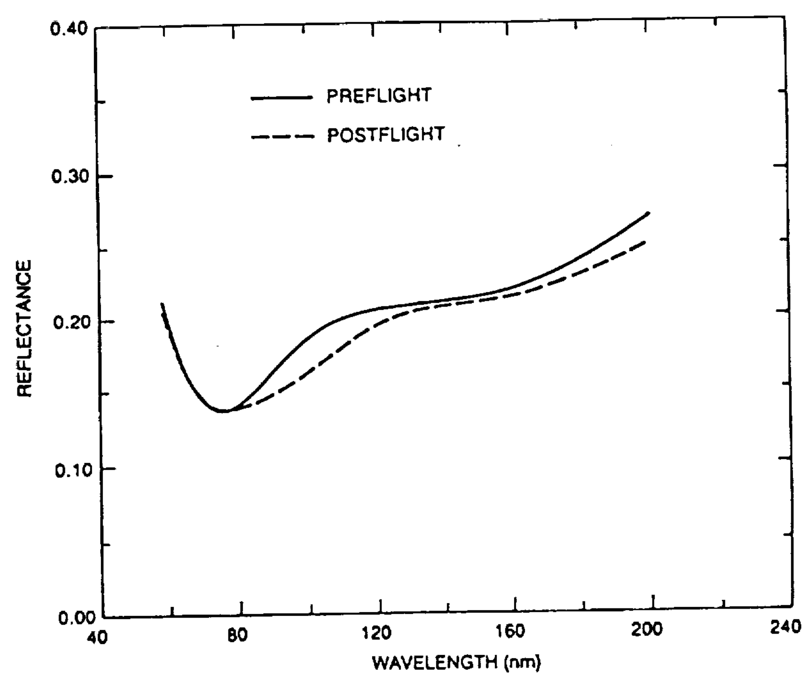

Figure 4. Effect of long duration, low earth orbit exposure on the VUV reflectance spectrum of a platinum film.

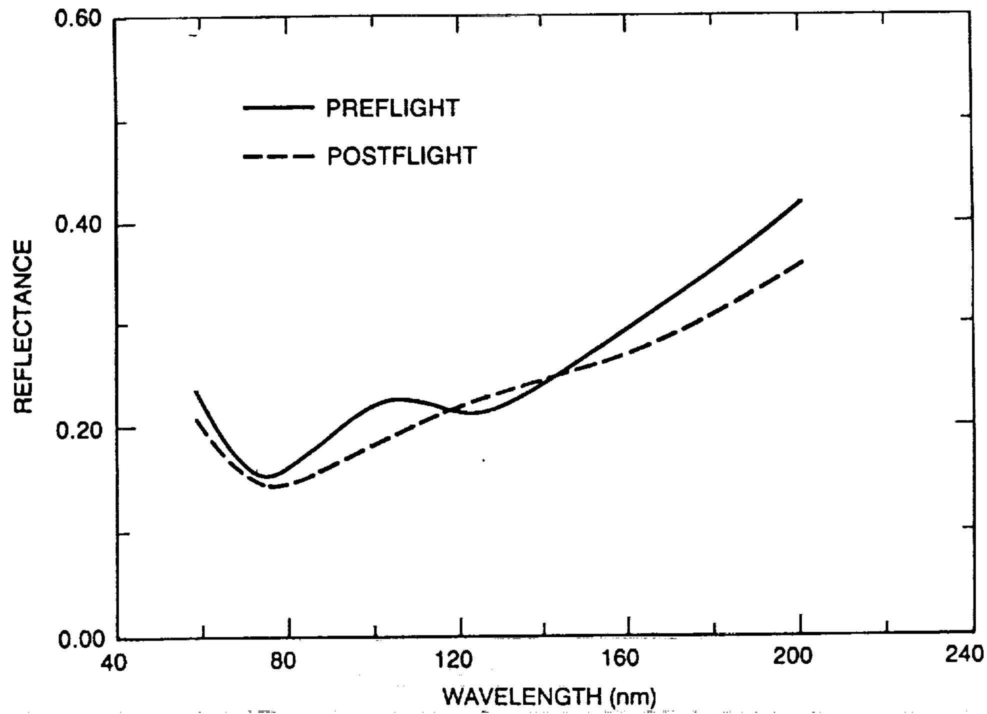

Figure 5. Effect of long duration, low earth orbit exposure on the VUV reflectance spectrum of an iridium film.

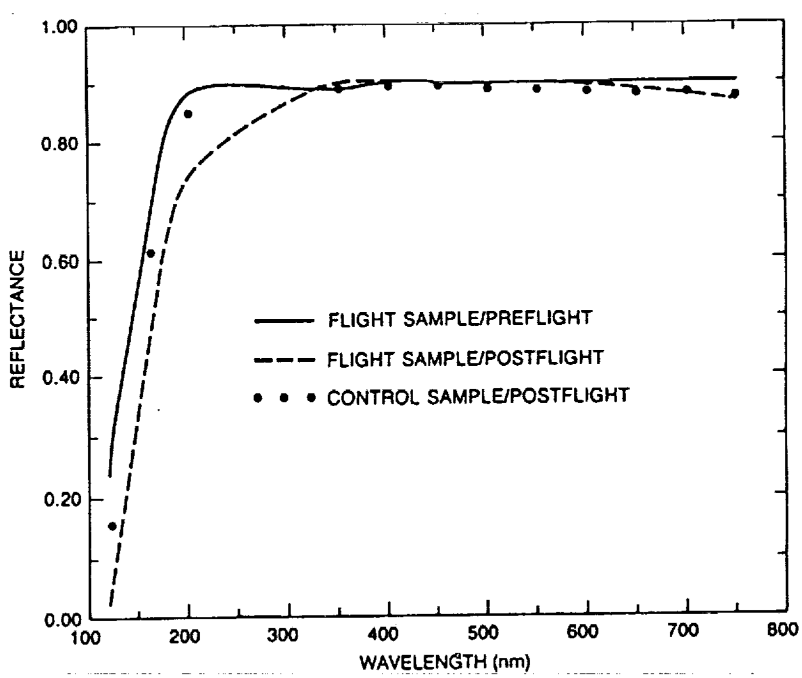

Figure 6. Comparison of VUV-through-visible spectra of the flight sample and a nonflight control sample of an aluminum film.

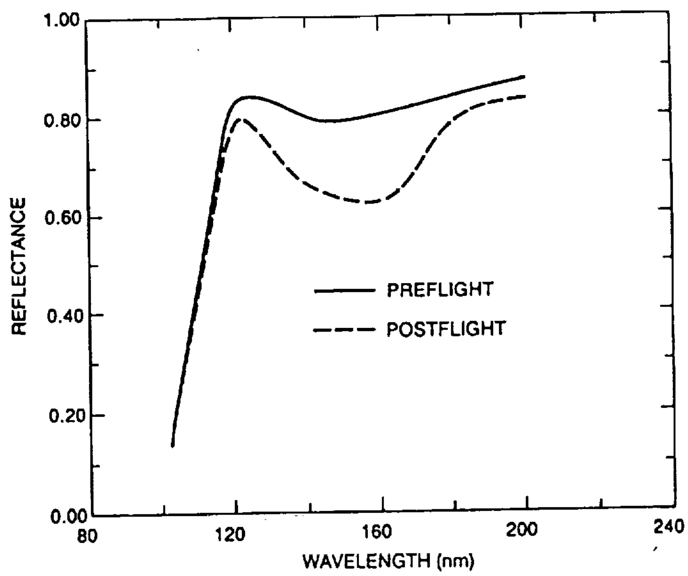

Figure 7. Effect of long duration, low earth orbit exposure on the VUV reflectance spectrum of a magnesium fluoride-overcoated aluminum film.

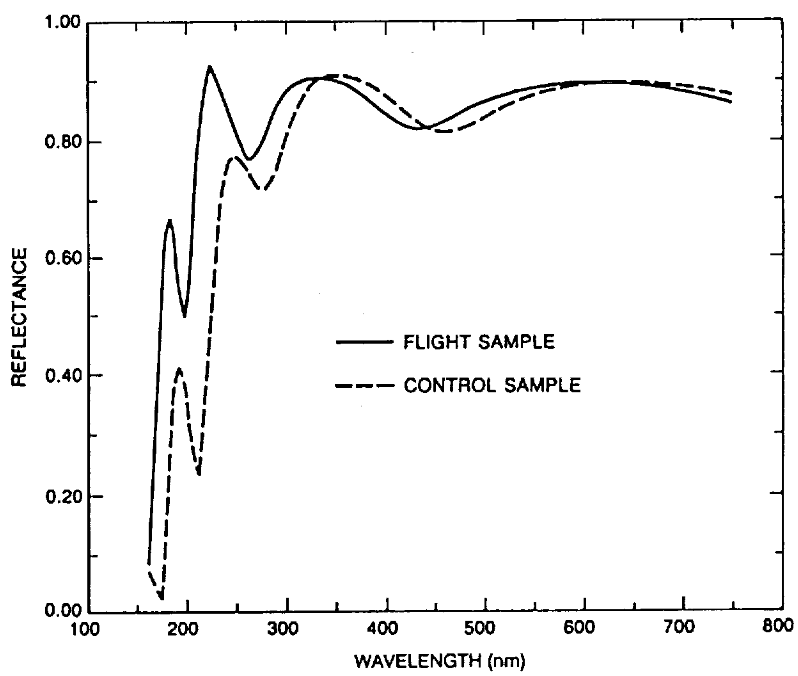

Figure 8. Comparison of VUV-through-visible spectra of the flight sample and a nonflight control sample of an aluminum film overcoated with reactively deposited silicon monoxide.

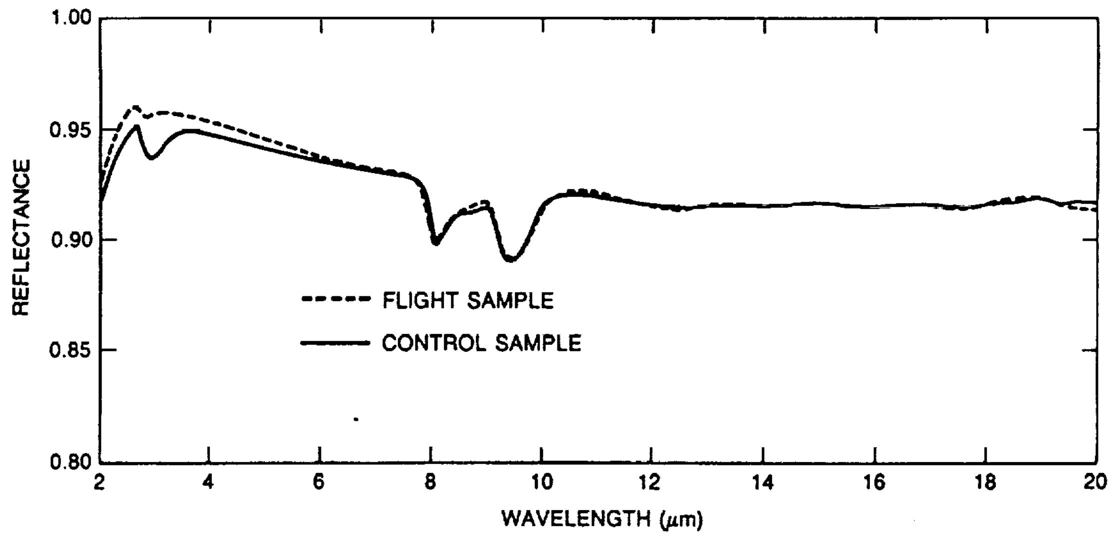

Figure 9. Comparison of infrared reflectance spectra of the flight sample and a nonflight control sample of an aluminum film overcoated with reactively deposited silicon monoxide.

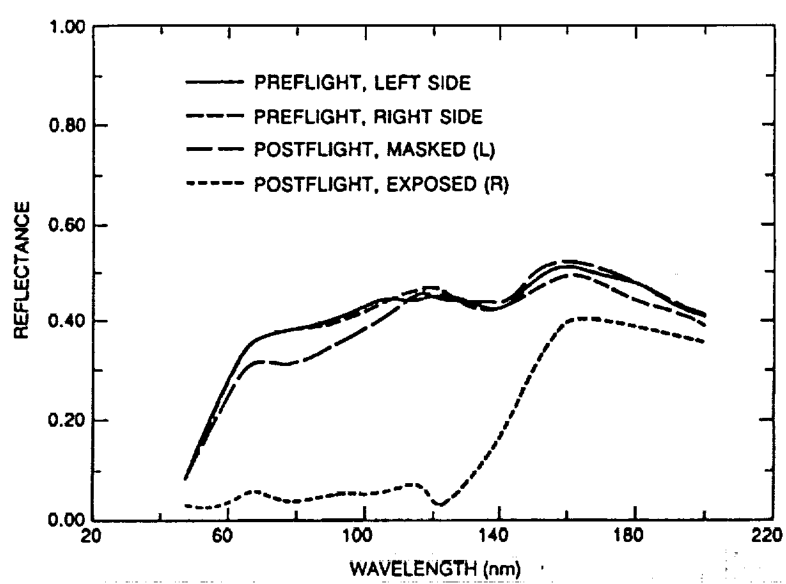

Figure 10. Effect of long duration, low earth orbit exposure on the VUV reflectance spectrum of exposed and masked portions of a CVD SiC sample mounted on the leading edge of the LDEF spacecraft.

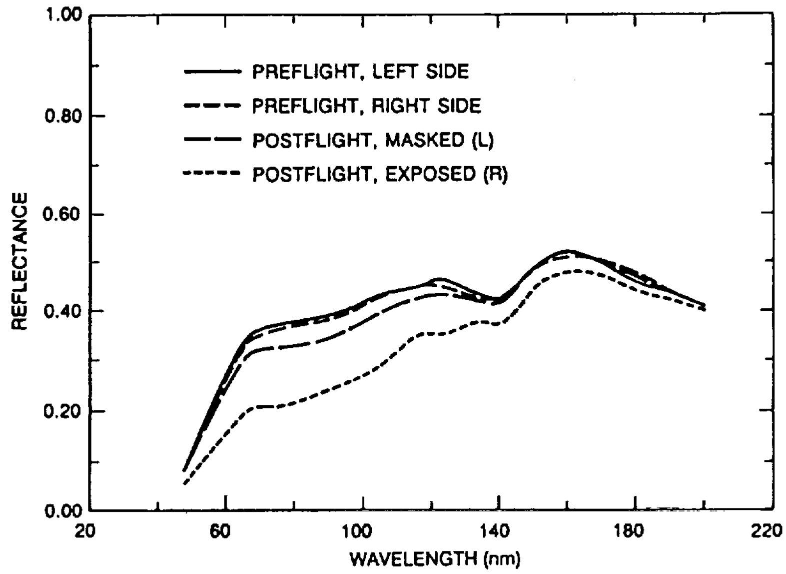

Figure 11. Effect of long duration, low earth orbit exposure on the VUV reflectance spectrum of exposed and masked portions of a CVD SiC sample mounted on the trailing edge of the LDEF spacecraft.